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The Action of Potassium Persulphate
on the Halogen Acid Salts

Chemistry

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THE ACTION OF POTASSIUM PERSULPHATE
ON THE HALOGEN ACID SALTS

BY

RALPH PILLSBURY GATES

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1912

1917
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UNIVERSITY OF ILLINOIS

June 1st 1912

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Ralph. Pittsburry Gates

ENTITLED The Action of Potassium Persulphate
on the Alkali Salts of the Halogen Acids

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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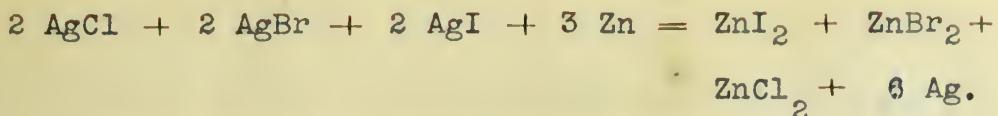
The Action of Potassium Per sulphate on the
Halogen Acid Salts.

When a perfectly neutral solution, containing the alkali salts of the halogen acids, is treated with an excess of potassium persulphate, the iodide only is oxidized, and iodine liberated, while the bromide and chloride are unattacked. If the solution is acidified, the chlorine alone remains unattacked provided the concentration of the acid is kept below two times normal. These facts would seem to furnish a satisfactory basis for the separation of these halogen elements.

As a means for the qualitative detection of chlorides, bromides, and iodides in the presence of each other, this method has been recommended by Willard; and the details of the procedure may be found in the appendix of Prescott and Johnson's qualitative chemistry. Failure to detect considerable quantities of bromide in the presence of iodide by this method, however, renders it of doubtful value.

The generally accepted equations that represent these reactions are,





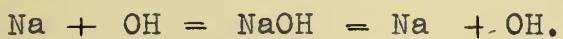
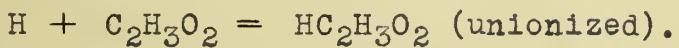
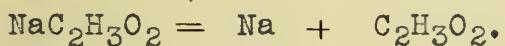
The quantitative separation of chloride, bromide, and iodide is discussed by R. Engel¹. He gives the following, "Ammonium persulphate can easily be used for the separation of bromine and chlorine by heating the mixture to a temperature of about sixty or seventy degrees Centigrade, and conducting the liberated bromine, by an air stream, through a dilute solution of sulphurous acid. The separation is completed in about one hour, and is a quantitative one. Since in the decomposition of the persulphate by heat, there is some ozone formed that would liberate iodine from a solution of potassium iodide, this cannot be carried out in the presence of iodides. Ammonium persulphate may be used, however, for the separation of the iodine from a mixture of the iodide, bromide, and the chloride, if one treats such a mixture with ammonium persulphate in the presence of sodium acetate. All the iodine will be set free without any of the bromine or the chlorine being liberated. The iodine may be absorbed in a suitable solution and titrated with sodium thiosulphate".

An article of the same nature appeared in the Proceedings of the Royal Society of France², presented by M. Friedel,

¹ "Ausgewahlte Methoden der Analytischen Chemie", von Dr. H. Clas-
sen, page 414.

² Compt. rend. 118, 1263 (1894).

and referring to the article of Engel's to which I have referred, he says that the persulphate of ammonia may be used for the separation of iodine in the presence of the chloride and bromide. His words are, "In the cold and in the presence of sodium acetate all the iodine of the iodide is set free by the persulphate, without liberating the smallest trace of bromine or chlorine. The iodine is not able to be set free quantitatively in a hot solution, because it will form a certain quantity of hydriodic acid. Therefore one must work in the cold, and may extract the iodine with the aid of carbon bisulphide and titrate with sodium thiosulphate". The meaning of these statements is that in a slightly alkaline solution due to the presence of the sodium acetate which hydrolyses thus,



the iodine from a mixture of the iodides, bromides, and chlorides can be quantitatively separated by the use of ammonium persulphate in a cold solution.

In an article published in the Proceedings of the Royal Society of Edinburgh¹, entitled, "Action of Persulphates on Iodine" by Hugh Marshall, the following statements appeared;

¹ Volume II, Page 388 (1898-99).

"When solutions of potassium persulphate and potassium iodide are mixed, iodine is liberated and potassium sulphate is formed. The action takes place somewhat slowly in the cold, but much more rapidly on warming. It has generally been supposed that the reaction,



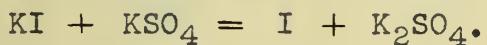
completely represents the reaction that takes place, and although I have had occasion to try the reaction very many times, since I first noticed it as a reaction of persulphates, it was only a year ago that I observed a further change. On boiling a solution of potassium iodide with ammonium persulphate in order to decompose it and drive off the iodine by sublimation, it was observed that the free iodine in the liquid seemed to disappear very rapidly, more so than corresponded to the amount volatilised, and that the final disappearance took place with unexpected suddenness. This pointed to the possible conversion of the iodine into some other compound, probably by the oxidising action of the persulphate. This proved to be the case, because, on the cautious addition of sulphurous acid to the colorless solution, iodine again appeared; and on standing the solution again became decolorised, and was once more turned brown on the addition of sulphurous acid. These actions could be repeated so long as there was any persulphate in the solution. The action takes place slowly in the cold, and at high temperatures there is considerable volatilisation of iodine; when a solution of potassium iodide was corked up with am-

monium persulphate at ordinary temperatures, the iodine which separated in the solid form, gradually dissolved on standing, and in a few days entirely disappeared. The oxidation product was not investigated further at that time, it was assumed to be iodic acid.

Some months later, attention was called again to the subject by the appearance of an abstract of a paper on the determination of chlorine, bromine, and iodine in organic compounds, by distilling the substance with a mixture of sulphuric acid and persulphate. The possible oxidation of iodine under these conditions was apparently overlooked, and the method may therefore not be so active for that substance as for chlorine and bromine. It became necessary to study some of the product of the reaction to definitely settle its composition. This was done by digesting in an erlenmeyer flask four or five grams of iodine and a sufficiently strong solution of ammonium persulphate to convert all the iodine to periodate. The loosely corked flask was placed on a heating coil, so that its temperature varied from ten to fifteen degrees during the night, and from thirty to thirty-five during the day. In the course of fully a week the whole of the iodine was dissolved and oxidised, and in its place there was a moderate quantity of a white crystalline solid. This was separated, washed, and recrystallized from hot water. Its solution was strongly acid, free from sulphate, and gave all the reactions of an iodate and of an ammonium salt. It was evidently am-

monium hydrogen iodate. The original mother liquor containing chiefly ammonium hydrogen sulphate was neutralized with an ammonium solution, whereupon a white crystalline precipitate separated out, which was probably normal ammonium iodate. In order to prove conclusively that it was iodate and not the periodate its oxidising power was determined by means of potassium iodide and sulphuric acid, the liberated iodine being titrated with a standard solution of sodium thiosulphate. The results were compared with those of pure ammonium iodate, prepared by other methods. It was found that 0.1540 grams of substance corresponded to a volume of thiosulphate solution equivalent to 0.1534 grams of ammonium iodate. There is no doubt therefore that the persulphate oxidises the iodine to iodic acid".

T.S. Price¹ in a paper concludes that the reaction is one of the second and not of the third order as was anticipated. Then the reaction would be



rather than,



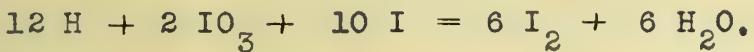
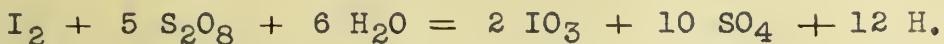
According to Marshall there would be some doubt as to this, because all the solutions used were very dilute and it is not possible to say what effect the liberated iodine would have on the rate of decomposition. There may be a certain amount of catalytic action, the iodine being alternately oxidised by

¹ Zeit. fur Phys. Chemie, XXVI, p.474 (1898).

the persulphate and reduced by the hydriodic acid, and the reaction may not be the simple one represented by the equation,



but may really be the much more complex one represented by the equations,



The purpose of this investigation is to study quantitatively the reactions between the salts of these halogen acids and potassium persulphate, and to employ it, if possible, as the basis of a method for the quantitative separation of chlorine, bromine, and iodine from a mixture containing all three.

From the statements of Engle and Marshall it would seem as if iodine could be liberated quantitatively from an alkaline solution of its salts, and that were bromine present in the same mixture, it would not be liberated. In order to study this reaction, a small quantity of potassium bromide was dissolved in varying concentrations of potassium hydroxide, potassium persulphate was added, and the solution heated in a water bath. A stream of air through the solution carried any liberated bromine into a solution of potassium iodide which contained a little starch. The apparatus used consisted of a round bottomed flask provided with a three holed rubber stopper, through which was fixed a capillary tube for the air and a bent tube which led into a filter flask containing a solution of potassium iodide. The flask was connected to a filter pump. The results obtained were as follows:

| KOH Conc. | Temp. | Result |
|-----------|---------|--------|
| 0.1 N. | boiling | No Br. |
| 0.5 N. | " | " |
| 0.25 N. | 60 Deg. | Br. |

In the action of the potassium persulphate there is some ozone liberated and this would cause a blue coloration of the starch iodide solution. For this reason a new arrangement was made. The starch iodide solution was replaced with a solution of potassium hydroxide and the iodine was absorbed in this solution. Sulphur dioxide was passed through the solution and silver nitrate was added. The result showed that there had been some iodine liberated, as a precipitate of silver iodide was formed.

Several trials were made using an alkaline solution of potassium iodide and a bath heated to about forty to fifty degrees centigrade. In each case there was considerable difficulty in even liberating a part of the iodine, the reason for which will be evident by a consideration of the mass action equation that governs this reaction.



$$\frac{(I_2)(OH)}{(HIO)(I)} = K.$$

The value for K is known to be 10^{-5} #. Allowing an error of .2 of one per cent for the iodine in the form of HIO the concentration of the hydroxyl ion that fulfills the equation is calculated to be about ten to the minus fourteenth power, which is smaller than the hydroxyl concentration of pure water.

#Sammet, Zeit. Physik. Chem., Vol. 53, p. 641.

Using a one molal solution of sodium acetate, the following calculations will show the value for hydroxyl concentration and also for the amount of iodine lost in the HIO formed. The equation for the hydrolysis of the salt of a weak acid is,

$$\frac{K_w}{K_a} = \frac{h^2 C_s}{1-h},$$

where K_w equals the ionization constant of water at temperature of the experiment, K_a equals the ionization constant of the acid, h equals the degree of hydrolysis, and C_s equals the original concentration of the salt. The temperature in this experiment is about eighteen degrees, for which K_w equals .5 times 10^{-14} , K_a equals 1.8 times 10^{-5} , and C_s equals 1. h figures out to be .00017. The concentration of the hydroxyl ion equals the degree of ionization of the base, NaOH, multiplied by the degree of hydrolysis, and the total concentration of the salt $\text{--}(\text{OH})$ equals $B^h C_s$. Such a base is ionized to about 80 per cent. The hydroxyl ion concentration figures out to be 1.36 times 10^{-4} .

Using this concentration in the equation,

$$\frac{(\text{I}_2) (\text{OH})}{(\text{HIO}) (\text{I})} = 10^{-5},$$

and letting (HIO) and (I), which are formed in equimolar quantities equal X, HIO equals .0064, or the I in grams equals .0081 which is a loss of 4.2 per cent.

Repeating these calculations with a .1 molal solution of the salt,

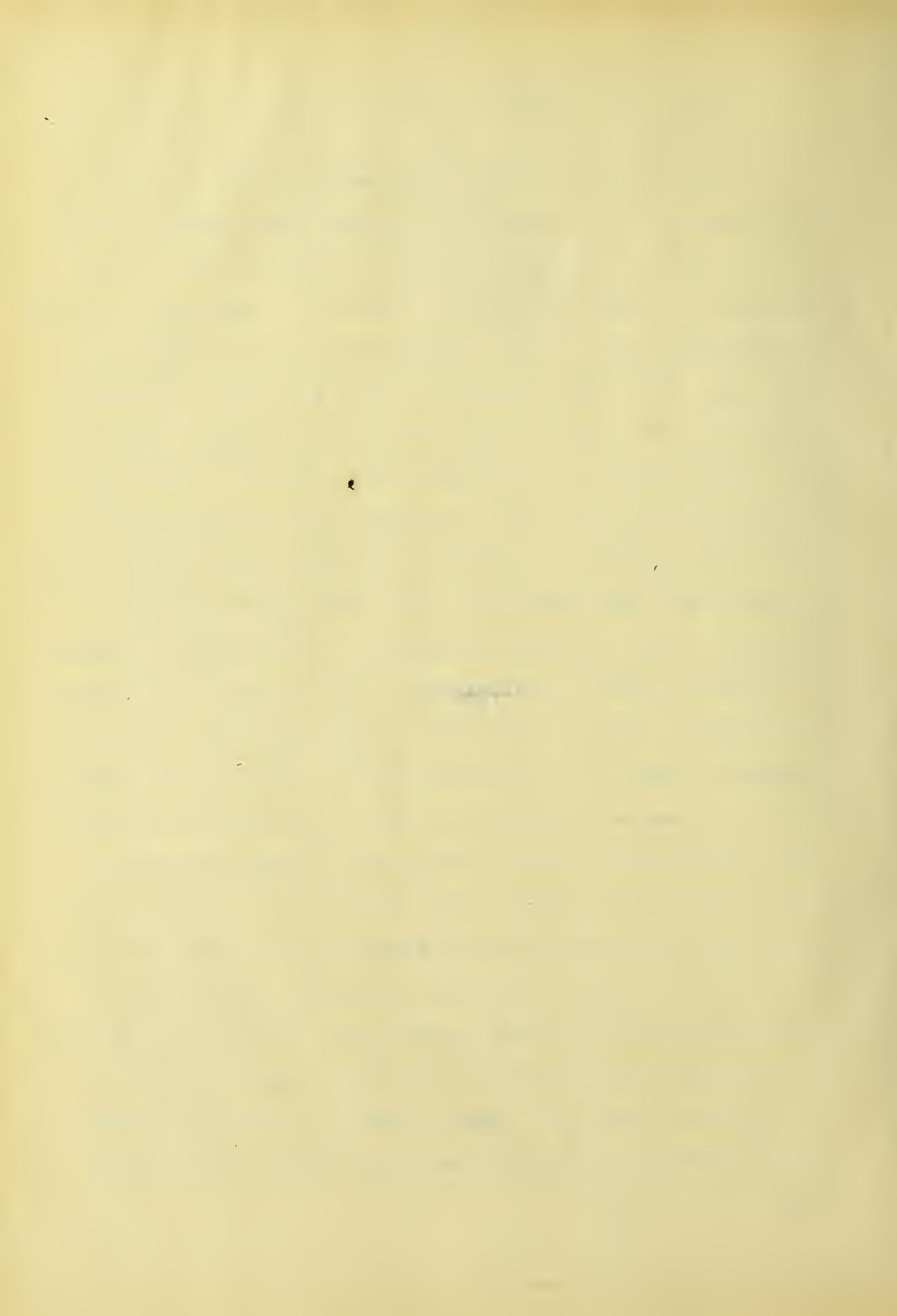
Hydroxyl Conc. equals .0424 times 10^{-4}

Moles HIO " .00007

Grams I equals .000888

% lost " .49

These results show that the amount of HIO formed by the oxidation of the iodine is too great in an alkaline solution of greater basidity than water to allow a quantitative separation of iodine from one of its salts. This would explain why the iodine was not all liberated from the alkaline solution used. From these results it would seem that the separation was not carried out successfully in an alkaline solution, and to gain additional facts about the reaction it was studied in a neutral solution. The potassium iodide was dissolved in water, and an excess of potassium persulphate was added. The apparatus was then connected to the pump and the suction turned on. The reaction was carried out in the cold to lessen the possible chance of oxidation. It was a very slow reaction, taking several days for the color in the original solution to disappear. When, to all appearances, the reaction was completed, the potassium hydroxide solution of the iodine was saturated with sulphur dioxide, generated by dropping sulphuric acid on potassium sulphite. The solution was acidified with nitric acid, and silver nitrate added to precipitate the iodine as silver iodide. The silver iodide was filtered in a previously weighed platinum crucible, and the amount of iodine was calculated and compared to the amount that should have been liberated from the original amount of potassium iodide, if the potassium persulphate had acted only as a liberating agent.



The following result was obtained:

| Purity of Sample: | Wt. KI | Theor. I | Calc. I | % Purity |
|-------------------|----------|----------|----------|----------|
| | .1816gr. | .1389gr. | .1382gr. | 99.5 |

| Wt. KI | Wt. AgI | Theor. I | Calc. I | % Error |
|----------|----------|----------|----------|---------|
| .2528gr. | .3535gr. | .1922gr. | .1911gr. | .57 |

As there were some difficulties in performing this as described, a solution of potassium iodide was substituted for the solution of potassium hydroxide. The iodine was absorbed in this solution and titrated with a standard solution of sodium thiosulphate, using starch as an indicator. The results obtained were:

| Wt. of KI | Wt. K S O ₂ ₂ ₈ | cc. Na ₂ S ₂ O ₃ | Theor. I | Calc. I |
|-----------|--|---|-----------|----------|
| .1358gr. | .4831gr. | 6.60 | .1033 gr. | .0944gr. |

| % Error | Time of run |
|---------|-------------|
| 8.6 | 30 Hours |
| 15.5 | 24 " |

In the first case one absorbing flask of potassium iodide was used. This did not seem to be enough as there was no means of telling whether there had been a loss of iodine as the potassium iodide solution became saturated. To avoid this, four bottles of potassium iodide solution were used in the second case, and in this way any iodide drawn over by the air was absorbed in the next solution. Even four bottles did not seem to be enough, as there was a tendency for the iodine to be

drawn over farther and farther as the time of the run increased. For this reason, a new method was devised for collecting the iodine.

The iodine was liberated in a separatory funnel, in which was a solution of carbon tetrachloride. As the iodine was liberated it was absorbed in the carbon tetrachloride solution. When this solution became saturated, it was withdrawn and a fresh sample was added. This was repeated until all the iodine was liberated as shown by the color of the water solution, and until all the iodine thus liberated was absorbed in the carbon tetrachloride, as shown by the absence of color in the successive washings of the solution with carbon tetrachloride. To the flask containing the iodine in the carbon tetrachloride, a solution of potassium iodide was added. The iodine being more soluble in potassium iodide than carbon tetrachloride, was taken up by the potassium iodide and was titrated with a standard solution of sodium thiosulphate. This was carried out, using starch as an indicator, with the following results:

| Wt. KI | Wt. $K_2S_0_2S_8$ | cc. CCl_4 | cc. $Na_2S_0_3$ | Theor. I | Calc. I | % Error |
|----------|-------------------|-------------|-----------------|-----------|-----------|---------|
| .1022gr. | .2273gr. | 100 | 5.31 | .07922gr. | .07591gr. | 4.1 |
| .1300 " | .2906 " | " | 6.75 | .10077 " | .09655 " | 4.1 |
| .1508 " | .5044 " | " | 7.75 | .1168 " | .1071 " | 8.3 |
| .1150 " | over .3" | " | 6.19 | .08914 " | .08556 " | 3.9 |
| .1311 " | over .3" | " | 6.67 | .1016 " | .0912 " | 10.2 |

These results seem to show that the reaction does not proceed in a quantitative fashion. However, the rest of the

iodine must be in the solution in some form, and in order to find out somewhat more definitely the reaction was studied in this way. The first step in the reaction was carried out as before, and the remaining solution was reduced with sulphur dioxide, which would reduce any iodine that had been oxidized to iodic acid. The solution was made acid with nitric acid and silver nitrate was added to precipitate the iodine. There seemed to be a yellow precipitate , which might have been silver iodide, that came down on first addition of silver nitrate, but the heavy precipitate of silver sulphate that quickly appeared obscured it. Enough silver nitrate was added to precipitate such a quantity of iodine as could be present, the solution filtered, and washed free from sulphate. The result was of little value as it was so difficult to wash free from sulphate and as it took such a long time. There seemed to be an indication that there was some of the iodine as iodic acid. Another method with the same end in view was tried. The solution containing the unaccounted for iodine was reduced with sulphur dioxide as before and the excess was boiled off, and a small amount of potassium persulphate was added. A color resulted in the carbon tetrachloride solution which showed that there was at least some of the iodine in the solution as iodic acid. This iodine was collected in the same way as before and determined by titrating with sodium thiosulphate.

The following results were obtained:

| Wt.KI | Wt. $K_2S_2O_8$ | cc. $Na_2S_2O_3$ | Theor.I | Calc.I | % Error |
|--------------------------------|-----------------|------------------|----------|-----------|---------|
| .1360gr. | .2594gr. | 7.13 | .1054gr. | .09855gr. | 6.5 |
| .1465 " | .3655 " | 7.65 | .1136 " | .10574 " | 6.9 |
| .1108 " | .2027 " | 5.85 | .08593" | .08086 " | 5.9 |
| .1142 " | .2504 " | 5.80 | .08852" | .08017 " | 9.4 |
| second addition of persulphate | | | | | |
| | | .05 | | .00069 | 5.8 |
| | | .05 | | .00069 | 6.2 |

In the case of the third and fourth results the additional amount of iodine was not of sufficient quantity to cause a return of the blue color to the starch solution.

These results show that some of the iodine in the solution is oxidized to iodic acid, but it would seem as if the greater part of the unaccounted for iodine was oxidized to some other form, perhaps the periodate. This could be proven by isolating some of the product and determining its chemical composition.

In reviewing the results of these investigations, together with a study of the mass action equilibrium represented by the equation,

$$\frac{(I_2) \cdot (OH)}{(HIO) \cdot (I)} = 10^{-5}$$

it is evident that if the concentration of hydroxyl ion is greater than that of pure water, the iodine will not be quantitatively liberated, due to the formation of too large a quantity of HIO. In a hydroxyl ion concentration of 4 times 10^{-6} , slightly greater than that of water, the error due to the formation of HIO would

be about one half of one per cent.

In a neutral solution, the results show that there is not a quantitative liberation of iodine, due to the probable oxidizing action of the persulphate. What this oxidation product is, was not definitely determined, and although a small part is undoubtedly iodic acid, the greater part appears to be in another form.

The reaction in either an alkaline or in a neutral solution is a very slow one, taking several days to liberate the iodine from a sample weighing two tenths of a gram. By heating the solution the oxidation is increased.

In view of all this it seems as if a quantitative method for the separation of iodine from a mixture of the halogen acid salts, using potassium persulphate as an oxidizing agent, cannot be successfully carried out.





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